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Study of unsaturated soil zone in sludge dump area at Digboi Refinery

Prepared for **Indian Oil Corporation Limited
(Assam Oil Division)
Digboi Refinery**

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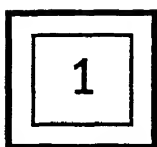
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(Banwari Lal, M S R Sastry, U Gangi Reddy, Vinod Kumar, Abu Swaleya and Samarjeet)



Introduction

Ground water table and subsurface soils are two major abiotic components of the ecosystem behaving as relatively stagnant nutrient source /sink and water pool respectively with very low turnover rate and hence with no potential reclamation chances once deteriorated. However, these two components have tremendous impact on ecosystem regulation with drastic biological and socio-economic consequences. With groundwater becoming the chief perennial source of drinking water particularly in urban/rural areas, and also contributing significantly to major agricultural and industrial needs there is an increased concern not only to preserve this perishable resource but also to maintain its virginity amicable to its dynamic utility index.

Acid tar oil sludge disposal is one of the major causes of concern in view of safeguarding stressed edaphic and shrinking water resources. Fortunately, bioremediation of oil sludge has been rendered extremely successful and technoeconomically feasible using microbial biotechnology, which has seen a major technological breakthrough (TERI, Patent No./Sanjeet et al, 2000, 2001). However, the impact of long term storage of acid tar sludge which is relatively non-degradable and stable pollutant in refuge ponds may have affected the adjacent and underlying soil bed and water resources critically.

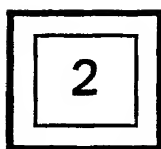
Sludge borne heavy metals from petroleum industry especially petroleum refineries are potential source of pollution. Heavy metals contamination arising from the sludge by leaching and percolation into adjacent soil horizons and water table could be of varying magnitude depending on the soil type, pH, porosity, size, depth of water table, precipitation and several other factors. Fifty elements are classified as heavy metals, 17 being considered toxic. As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn need special attention owing to their highly toxic biological manifestation. The bioavailability of these metals is highly pH dependent with higher availability at lower pH at which they are most reactive. By becoming incorporate with an organic component these metals become readily available to the first trophic level of food chain and eventually leading to

biological magnification through the system. As far as ground water is concerned it particularly has low availability as compared to any other water resources. The rate of quality change and contamination with these metals depend on the depth of sampling and size and porosity of the overlying soil horizons. These changes occur over a period of time depending upon the land use and percolation. As the ground water movement is highly restricted to only a few feet per year, there emerges local concentration pockets (contamination zones) with poor dilution of pollutants and hence a major threat to the community health with high dependency on ground water and linked aquifers for routine and other uses.

Hence, comprehensive studies, on the status of soil and water pollution levels caused by extended storage of acid tar sludge at Digboi Refinery, Assam, were made during the present course of investigation.

The objectives of the proposed ground water quality assessment programme were to:

- monitor the change in ground water quality over time along the upstream and downstream water pockets
- Ascertain a baseline to the ground water quality and its utility index for various purposes viz. potability and agricultural and industrial use and
- Delimit the adverse impact and penetration of the contaminated source into the hydrological cycle and entrance into the biotic system.



Study of unsaturated soil zone in sludge dump area at Digboi Refinery

Methods

Ground Water Pollution Monitoring

Water samples were collected from the 4 borewells installed east, west, north and south to acidic tar sludge pit (Fig. 1). The borewells were flushed out initially and the water collected in acid-washed polyethylene bottles. The samples were fixed with HNO_3 at a final concentration of 0.5%. pH of the water samples was recorded on spot prior to addition of HNO_3 . An aliquot without acid fixation was also collected.

Collection of Soil Samples

Soil samples, adjacent to the four borewells located along the 4 directions of acidic tar pit, were collected from the surface and subsurface (50 cm below the surface and 100 cm below the surface as shown in Fig. 1).

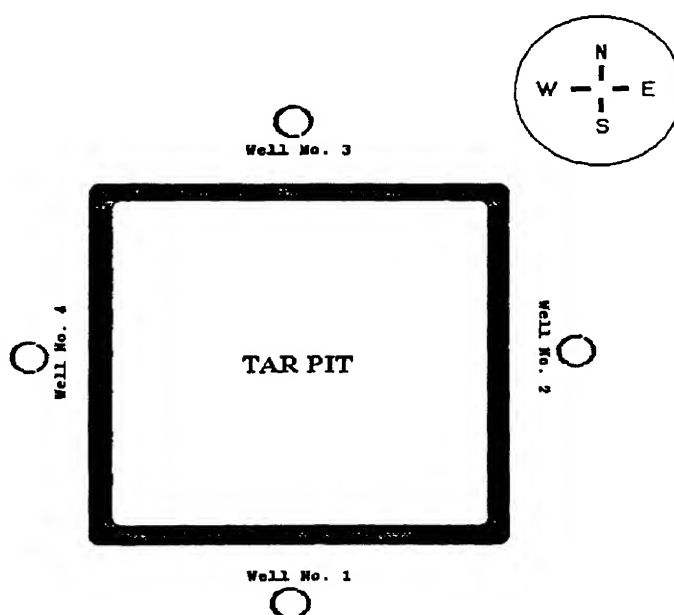


Figure 1. Digboi Refinery Tar pit sampling layout

Sample Analysis

The samples were analysed for the following quality assessment parameters:

- pH, Conductivity, oil/grease, BTX (benzene, toluene xylene) and
- Heavy metals- As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, V, Zn.

PH and Conductivity

pH of water samples was measured directly from the samples without addition of fixative. For soil pH, a 40% soil suspension in deionized Milli-Q water was prepared, mixed for 30 minutes and allowed to stand undisturbed for 2 hours and the pH recorded using a digital pH meter. Conductivity was measured using a conductivity meter. Soil conductivity was determined by preparing saturated slurry in deionized water.

BTX Analysis

Benzene, toluene and xylene in water and soil samples were analysed using Gas Chromatography.

Heavy Metal Analysis

As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V and Zn were analysed from water and soil samples using Atomic Absorption Spectrometry.

Digestion

The samples were digested with the help of MARS 5 (Microwave Accelerated Reaction System version 5) Supplied by CEM Corporation, USA. Digestion was completely closed digestion. Five ml of HNO₃ and 1 ml of hydrogen fluoride were used for digestion. The samples were diluted to required volume and then analysis was carried out.

Analysis

Analysis was carried out with the help of AAS- TJA (Unicam, USA) SOLAAR M Series Model fitted with Gilson Flame auto sampler with Auto Diluter and GF95 Graphite Furnace having FS 95 autosampler. Data was processed with SOLAAR M Data station S/W version 8.12, spectrometer S/ W version 1.14.

Wherever needed, matrix modification was performed to overcome the interference of the matrix.

Oil/Grease estimation

Oil/grease in water/soil samples were analysed by extraction of total petroleum hydrocarbon (TPH) from water/soil samples using organic solvent. Various fractions of oil/grease were analysed by GC using capillary column. Oil/grease were fractionated into alkane, aromatic, asphaltene and NSO (nitrogen, sulphur and oxygen containing compound) fractions with silicagel column. After dissolving oil/grease in n-pentane soluble and insoluble fractions (asphaltenes) were obtained. The alkane fraction was eluted with hexane, followed by the aromatic fraction that was eluted with benzene. The NSO was also eluted with chloroform and methanol. Further, alkane and aromatic fractions were concentrated by evaporation of solvents and then 0.2 µl of each was analyzed by gas chromatography (GC Hewlett Packard, 5890 Series II) to identify all the compounds present in the alkane and aromatic fractions. In the alkane fraction, various alkane compounds were identified by matching the retention time with authentic standards. Simultaneously, each alkane compound was confirmed by spiking the alkane fraction. A known amount of each standard alkane compound was added to the alkane fraction and injected into GC (co-injection) so that the peak area of each alkane compound increased as a result. Similarly, the polycyclic aromatic hydrocarbon compounds were identified by matching the retention time with an authentic standard and confirmed by spiking the sample with authentic standards.

Hydrocarbon degrading bacterial population in soil

Hydrocarbon degrading bacterial population was estimated in soil collected from different depths along four different wells. One gm soil samples were serially diluted in sterile saline water and aliquots of appropriate dilutions were plated out on minimal salt agar medium with crude oil/oily sludge as sole carbon and energy source. Hydrocarbon degrading bacterial colonies were counted and population of hydrocarbon degrading bacteria was estimated. Correlation was made whether bacteria present in soil are degrading hydrocarbon.

Note : All the instruments used for analysis of above parameter were calibrated

Results

pH and Conductivity

pH of the natural waters is partly determined by the geology of the watershed and is governed by CO₂/carbonate /bicarbonate equilibrium. pH plays a vital role in formation, alteration and dissolution of minerals and bioavailability of heavy metals and its use for consumption and other routine purposes. The electrical conductivity depends on the presence of ions, their total concentration and mobility. Conductivity could be empirically correlated to the total dissolved salts and also the purity assessment of drinking water.

A seasonal pH drift in the ground water was observed, during February 2001 being in slightly acidic range and in April 2001 at neutral. The electric conductivity (EC) was well within the range of drinking waters (Table 1).

Table 1 pH and conductivity of ground water samples collected during the months of February and April 2001 from bore wells situated on North, East, South and West site of acid tar pit

| Sample ID | PH* | | Electrical Conductivity** (mS/cm) | |
|------------|-----------|------------|-----------------------------------|------------|
| | Feb. 2001 | April 2001 | Feb. 2001 | April 2001 |
| Well No. 1 | 6.07 | 7.31 | 0.45 | 0.39 |
| Well No. 2 | 6.06 | 6.88 | 0.50 | 0.49 |
| Well No. 3 | 6.10 | 7.52 | 0.18 | 0.15 |
| Well No. 4 | 6.12 | 7.75 | 0.99 | 0.96 |

*BIS pH limits-6.5-8.5; **EC- Natural water ranges between 0.05-1.5 mS/cm

Soil pH in all the samples was slightly acidic and conductivity varied between 0.03-0.62 mS/cm (Table 2). No specific seasonal or stratified pattern was observed.

Table 2 Conductivity and pH of soils adjacent to acid tar pit during February and April 2001

| Sample ID | PH | | Electrical Conductivity (mS/cm) | |
|-------------------------------------|-----------|------------|---------------------------------|------------|
| | Feb. 2001 | April 2001 | Feb. 2001 | April 2001 |
| Soil samples near well No. 1 | | | | |
| Surface | 6.79 | 6.68 | 0.30 | 0.28 |
| 50 cm below surface | 5.45 | 5.33 | 0.21 | 0.17 |
| 100 cm below surface | 4.68 | 4.24 | 0.60 | 0.57 |
| Soil samples near well No. 2 | | | | |
| Surface | 5.30 | 5.37 | 0.06 | 0.03 |
| 50 cm below surface | 5.21 | 5.04 | 0.06 | 0.06 |
| 100 cm below surface | 7.20 | 6.20 | 0.27 | 0.21 |
| Soil samples near well No. 3 | | | | |
| Surface | 6.28 | 6.50 | 0.09 | 0.08 |
| 50 cm below surface | 6.36 | 6.77 | 0.05 | 0.08 |
| 100 cm below surface | 6.30 | 6.80 | 0.55 | 0.62 |
| Soil samples near well No. 4 | | | | |
| Surface | 5.20 | 5.15 | 0.21 | 0.25 |
| 50 cm below surface | 5.12 | 4.88 | 0.42 | 0.32 |
| 100 cm below surface | 6.00 | 6.28 | 0.46 | 0.46 |

Oil and Grease (ppm) from soil

Total petroleum hydrocarbon contamination levels in soil near acid tar were considerably high as shown in Table 3).

Table 3 Oil and grease content (ppm) from surface and subsurface soils of acid tar pit at Digboi Refinery

| Sample ID | February 2001 (ppm) | April 2001 (ppm) |
|-------------------------------------|---------------------|------------------|
| Soil samples near well No. 1 | | |
| Surface | 140 | 145 |
| 50 cm below surface | 600 | 420 |
| 100 cm below surface | 320 | 325 |
| Soil samples near well No. 2 | | |
| Surface | 160 | 200 |
| 50 cm below surface | 500 | 540 |
| 100 cm below surface | 440 | 490 |
| Soil samples near well No. 3 | | |
| Surface | 110 | 130 |
| 50 cm below surface | 640 | 320 |
| 100 cm below surface | 300 | |
| Soil samples near well No. 4 | | |
| | | 120 |
| Surface | 125 | 800 |
| 50 cm below surface | 710 | 250 |
| 100 cm below surface | 200 | |

However, oil and grease contamination were not traceable in ground water in any of the sampling bore wells and hence free of oil contamination.

Benzene, Toluene and Xylene (BTX) in Ground Water

Benzene, Toluene and Xylene were undetectable in ground water of sampling borewells at Digboi Refinery.

Hydrocarbon degrading bacterial population in Ground water and soil

Hydrocarbon degrading bacterial population was undetectable in the ground water samples indicative of oil contamination free ground waters. However, hydrocarbon degrading bacterial population in surface soil was 3×10^5 cfu/g soil. However, hydrocarbon degrading bacterial (aerobic bacterial) population could not be detected in soil samples collected from 50 cm and 100 cm depths near bore wells.

Heavy Metals

Although India owns a pollution regulatory authority but lacks a comprehensive enforcement law and structure to redefine the pollution norms from time to time. The Bureau of Indian Standards (BIS) has set certain permissible limits to each major pollutant but seems to be influenced grossly by the parameters set by World Health Organization (WHO) and US Environmental Protection Act (EPA) and Industrial Pollution Control (IPC) regulations. A brief perusal of the classification of the major pollutants shall be much relevant and revealing in the present context. UK had a Red list while US has List I and List II (Table 4).

Red List

The UK has produced a list (the Red List) of 23 substances to be subject to strict control for direct and indirect release to water. Such Red List substances are very strictly controlled. The substances are from the EC List I (Black List). In the UK the substances are prescribed under part I of EPA 1990, and listed in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991 (as amended) for the purposes of Industrial Pollution Control (IPC).

List I substances

List I (Black List) comprises 129 substances considered particularly harmful, priority being given to eliminating any pollution from them. The control of pollution from these substances is achieved through daughter directives which set out both the limit values and environmental quality objectives (EQOs) that Member States should meet. Thus the setting of standards for these substances is carried out at European level. A Department of Environment Circular (DoE 7/89) provides guidance on specific environmental quality standards and pollution limits.

List II substances

List II (Grey List) substances are considered less harmful when present in water than List I substances, but are still considered to have "a deleterious effect on the aquatic environment".

Table 4 This alphabetic table lists all metallic substances shown on any of EC Lists I (Black List) or II (Grey List) or on the UK Red List

| Substance | EC List I (Black List) | UK Red List | EC List II (Grey List) |
|-----------|------------------------|-------------|------------------------|
| Arsenic | X | X | |
| Boron | | | X |
| Cadmium | X | X | |
| Chromium | | | X |
| Copper | | | X |
| Iron | | | X |
| Lead | X | X | |
| Mercury | X | X | |
| Nickel | | | X |
| PH | | | X |
| Vanadium | | | X |
| Zinc | | | X |

Heavy metal content in water

Iron (Fe)

The form and solubility of iron in water depends on pH and redox potential of water. It is the formation of ferric oxide that makes iron-laden waters objectionable.

Between 6-9 pH natural unpolluted water rarely has iron content more than 1 ppm. However, Fe contents in all the samples were higher than the permissible limit (Table 5). In Well No.2 and 3 iron contamination was less in the month of February 2001, however iron contamination increased in the month of April 2001.

Table 5 Iron concentration in ground water along with bore wells situated on North, East, South and West sides of Acid tar pit

| Sample ID | Fe (ppm) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 24.20 | 19.53 | 0.3-1.0 ppm | Above permissible |
| Well No. 2 | 13.43 | 22.22 | | Above permissible |
| Well No. 3 | 15.00 | 22.34 | | Above permissible |
| Well No. 4* | * | 20.62 | | Above permissible |

**Well No. 4 not installed in February*

Chromium (Cr)

Chromium concentrations in natural waters are limited to very few μg . WHO recommendations set an upper limit of 5.0 ppb hexavalent chromium. At reduced pH hexavalent chromium converts into trivalent form. The Cr concentrations were high in all the wells in both the sampling periods (Table 6). There was no significant difference in Cr concentration in ground water during the month of February and April, 2001.

Table 6 Chromium concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Cr (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 9.50 | 8.10 | 5.0 ppb | Above permissible |
| Well No. 2 | 9.10 | 9.60 | | Above permissible |
| Well No. 3 | 7.30 | 8.30 | | Above permissible |
| Well No. 4* | * | 9.60 | | Above permissible |

**Well No. 4 not installed in February*

Nickel (Ni)

Nickel is known to be a key contaminant generated vastly by anthropogenic activities like fossil fuels usage and disposal. It occurs in combination with S, As and Ab. Nickel is usually absent from ground water. Nickel is present in form of a soluble salt and remains associated with suspended solids in combination with organic material. In presence of sulphur under anaerobic conditions it forms insoluble sulfides.

Ni is a hazardous contaminant and is an indicator of the impact of improper disposal of the petroleum wastes. The concentrations of Ni in ground water was higher than maximum permissible limit during the month of February and April rendering this water resource unfits for consumption (Table 7).

Table 7 Nickel concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Ni (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|----------|-------|-------------------------------|-------------------|
| | Feb. | April | | |
| Well No. 1 | 6.20 | 8.50 | 5.0 ppb | Above permissible |
| Well No. 2 | 7.30 | 7.80 | | Above permissible |
| Well No. 3 | 8.70 | 9.70 | | Above permissible |
| Well No. 4* | * | 6.25 | | Above permissible |

**Well No. 4 not installed in February*

Lead (Pb)

Lead salts are highly soluble in water and originate from a variety of anthropogenic activities including petroleum products. It is also toxic to aquatic organisms. WHO has set upper limits of 5.0 ppb for consumable water.

Lead concentrations were high in all the sampling borewells than the permissible upper limit in the months of February and April 2001 (Table 8).

Table 8 Lead concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Pb (ppb) | | BIS/WHO Permissible Limits | Comments |
|------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 6.30 | 7.70 | 5.0 ppb | Above permissible |
| Well No. 2 | 9.45 | 8.60 | | Above permissible |
| Well No. 3 | 7.10 | 7.90 | | Above permissible |
| Well No. 4 | * | 8.40 | | Above permissible |

**Well No. 4 not installed in February*

Zinc (Zn)

In water zinc is very scarcely soluble in both metallic and oxide form. It is present in trace quantities in ground water but in higher concentrations under acidic conditions. This element in excess quantities is not known to cause intoxication. It is an essential component in metabolism and required upto 4-10 mg per day. WHO has recommended a 5 ppm concentration for drinking water.

The Zn concentrations in groundwater of all sampling borewells are ranging between two-three times higher as per WHO standards. However Zn concentrations were within the permissible limit of BIS standards. Zn concentrations in ground water of all sampling borewells were stable in the months of February and April 2001 (Table 9).

Table 9 Zinc concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Zn (ppm) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 8.67 | 9.60 | 5.0-15.0/5.0 ppm | Above permissible |
| Well No. 2 | 11.93 | 11.11 | | Above permissible |
| Well No. 3 | 12.40 | 11.63 | | Above Permissible |
| Well No. 4* | * | 12.13 | | Above Permissible |

**Well No. 4 not installed in February*

Cadmium (Cd)

Ground water contamination with cadmium (Cd) has been witnessed widely and is not only toxic but also considered to be carcinogenic causing human prostrate carcinoma. A specific disease called "itai-itai" has been observed in Japan where high cadmium concentrations in water and crops are a persistent problem. Bioaccumulation in edible aquatic organisms and plants may be hazardous to ultimate consumer.

In the month of February and April 2001 Cd concentration in ground water of all sampling were higher than the permissible limits of BIS and WHO. All the sampling borewells including Upstream were also contaminated (Table 10). Proper care must be taken to avoid the release and circulation this Cd contaminated water pool into the over ground/terrestrial ecosystem.

Table 10 Cadmium concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Cd (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|----------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 3.70 | 3.65 | 1.0 ppb | Above permissible |
| Well No. 2 | 1.40 | 3.50 | | Above permissible |
| Well No. 3 | 2.30 | 2.90 | | Above permissible |
| Well No. 4* | * | 3.4 | | Above permissible |

**Well No. 4 not installed in February*

Copper (Cu)

Cu is an essential nutrient required by many enzymes for their activity and metabolic regulation. As it is poorly soluble in water Cu toxicity is rarely witnessed. The response to toxic Cu levels varies greatly with organism. Higher levels in water may develop undesirable bitter taste and render it unusable for domestic purposes.

Copper contamination in ground water of all the four wells were within permissible limits (Table 11).

Table 11 Copper concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Cu (ppm) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|----------------------------|-------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 0.03 | 0.25 | 0.5-1.0 ppm | Permissible |
| Well No. 2 | 0.71 | 0.64 | | Permissible |
| Well No. 3 | 0.12 | 0.15 | | Permissible |
| Well No. 4* | * | 0.18 | | Permissible |

**Well No. 4 not installed in February*

Arsenic (As)

Arsenic occurs in natural waters as arsenate (AsO_4^{3-}) and arsenite (AsO_2^-). Ingestion of ~ 100 ppm can cause severe toxicity and can also result from slow build-up of As concentrations in body.

There was no surprising elevation in as concentration of arsenic in ground water of all four wells during February to April 2001. Arsenic concentration in ground was higher or at par with the permissible limits in the month of February 2001. Increase in concentration above the limits, particularly of this element, leads to hyper-manifestation of the symptoms. This element is known to possess a bio-accumulation tendency and hence this water is not recommendable for general use (Table 12). Also it is practically and economically not feasible to clean-up the source, but further contamination shall be prevented.

Table 12 Arsenic concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | As (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 5.47 | 6.20 | 5.0 ppb | Above permissible |
| Well No. 2 | 9.98 | 10.40 | | Above permissible |
| Well No. 3 | 6.59 | 7.20 | | Above permissible |
| Well No. 4* | - | 7.00 | | Above permissible |

**Well No. 4 not installed in February*

Manganese (Mn)

Manganese usually is present in form of oxides or hydroxides and helps in control of concentration of various trace metals present in natural water system. Above, a 0.05 mg/L concentration it renders the water supply unsuitable for industrial applications such as those of textile dyeing, food processing, distilling and brewing, paper, plastic and photographic industries.

There is a clear indication of Mn concentration build-up in the ground water as the well No. 1 had potentially high concentration of this metal (Table 13). Sampling borewell no. 4 also had high concentration in the month of April 2001. Manganese concentrations were just at the margin of permissible limit in ground water of well no's 2 and 3.

Table 13 Manganese concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Mn (ppm) | | BIS/WHO Permissible Limits | Comments |
|-------------|----------|-------|-------------------------------|-------------------|
| | Feb. | April | | |
| Well No. 1 | 3.77 | 3.09 | 0.1-0.3/0.1 | Above permissible |
| Well No. 2 | 0.23 | 0.64 | | Above permissible |
| Well No. 3 | 0.24 | 0.19 | | Permissible |
| Well No. 4* | * | 2.31 | | Above permissible |

**Well No. 4 not installed in February*

Cobalt (Co)

Cobalt is not profusely toxic. It is about as virulent as iron and is almost as important to the body, especially liver. Cobalt is necessary for the production of vitamin B-12. About 3-4 µg of cobalt in the form of a biologically processed "salt" is essential to provide enough cobalt to sustain the body's B-12 level. However, excessive administration of this trace element produces goiter and reduced thyroid activity.

The Cobalt concentrations are ranging between 2.92 ppb to 7.20 ppb (Table 14). As observed in the month of February 2001, the concentration of Cobalt in ground water of well No's 1,2 and 3 were particularly higher in February as compared to April 2001.

Table 14 Cobalt concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Co (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 6.70 | 2.81 | 3-5 ppb | Permissible |
| Well No. 2 | 7.20 | 3.37 | | Permissible |
| Well No. 3 | 5.60 | 2.92 | | Permissible |
| Well No. 4* | * | 2.93 | | Permissible |

**Well No. 4 not installed in February*

Selenium (Se)

The maximal tolerable level of selenium in horses is estimated at 2 mg/kg of diet and the LD50 for orally administered selenium is considered to be approximately 3.3 mg of selenium (as sodium selenite)/kg of body weight. Apparent blindness, head pressing, perspiration, abdominal pain, colic, diarrhea, increased heart and respiration rates, and lethargy characterize acute selenium toxicity. This element is biologically accumulated. Selenium concentrations in ground water in bore wells near acid tar pit were high in February 2001 as well in April 2001 and could cause severe intoxication owing to its accumulation tendency in liver and body tissue (Table 15).

Table 15 Selenium concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | Se (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|----------|-------|----------------------------|-------------------|
| | Feb. | April | | |
| Well No. 1 | 2.40 | 2.65 | 0.5 ppb | Above permissible |
| Well No. 2 | 2.10 | 1.20 | | Above Permissible |
| Well No. 3 | 1.50 | 3.79 | | Above permissible |
| Well No. 4* | * | 2.89 | | Above permissible |

**Well No. 4 not installed in February*

Vanadium (V)

Reports of possible carcinogenicity by Vanadium are available. Dietary intake of vanadium is generally in the range of 10-30 µg/day. Most drinking-water samples contained less than 10 µg/litre.

Vanadium concentration in ground water of all bore wells situated near acid tar pit was within the permissible limit (Table 16).

Table 16 Vanadium concentration in ground water along with bore wells situated on North, East, South and West side of acid tar pit

| Sample ID | V (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|-------------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 2.16 | 3.52 | 5.0 ppb | Above Permissible |
| Well No. 2 | 2.08 | 2.19 | | Above Permissible |
| Well No. 3 | 1.80 | 2.70 | | Above Permissible |
| Well No. 4* | * | 3.90 | | Above Permissible |

**Well No. 4 not installed in February*

Molybdenum

Molybdenum is an essential element with relatively low toxicity. Molybdenum-containing enzymes catalyze basic metabolic reactions in the nitrogen, sulfur, and carbon cycles. Molybdenosis (teart) is a form of molybdenum toxicity that produces a disease in ruminants similar to copper-deficiency. Too much Mo will also interfere with the Cu containing enzymes. Little data are available on the human toxicity of molybdenum

The Mo concentration was found to be moderately above the permissible limits in February 2001 and April 2001 (Table 17).

Table 17 Mo concentration in the ground water along with bore wells of upstream and downstream samples of acid tar pit

| Sample ID | Mo (ppb) | | BIS/WHO Permissible Limits | Comments |
|-------------|-----------|------------|----------------------------|-------------------|
| | Feb. 2001 | April 2001 | | |
| Well No. 1 | 2.40 | 1.81 | 1.0-1.5 ppb | Above permissible |
| Well No. 2 | 3.17 | 2.80 | | Above permissible |
| Well No. 3 | 2.40 | 1.08 | | Permissible |
| Well No. 4* | * | 3.15 | | Above permissible |

**Well No. 4 not installed in February*

Analysis of Drinking water at Digboi Town

Drinking water at Digboi Town also monitor to compare the contamination levels in ground water at acid tar pit. Four sites were selected to monitor drinking ground water in Digboi Town.

Site 1:

Raw water was collected from water supply from well no. 10. Concentrations of all the heavy metals in raw water of well 10 was within the permissible limits except Iron. (Table 18).

Site 2:

Raw drinking water from well no. 13 was collected from water supply tank near Vishnu Mandir at new settlement area in Digboi town. Heavy metal concentrations in raw water of water supply tank near Vishnu Mandir at Digboi town was within the permissible limits. However, Iron concentrations were above the limits stipulated by WHO and BIS (Table 18)

Site 3:

Raw water (without treatment) was also collected from another water supply tank near shiv mandir at new settlement area. Iron concentrations in raw water were above the permissible limits. However, concentrations of other heavy metals were within the permissible limits (Table 18).

Site 4:

Drinking water sample was collected from a hand pump in Hoking para area at Digboi town. Iron concentrations in ground water samples collected from a hand pump were above the permissible limits stipulated by WHO and BIS (Table 18).

Table 18 Oil grease and other pollutants in ground drinking water at Digboi Town

| Parameter | Water supply Well No. 10 | New Settlement area Near Vishnu Mandir Well No. 13 | New Settlement area (near Shiv Mandir) | Hand Pump in Hoking Para | BIS / WHO Permissible Limits |
|-----------------------|-----------------------------|--|--|-----------------------------|---------------------------------|
| PH | 6.83 | 6.69 | 6.63 | 7.57 | 6.5 - 8.5 |
| EC (mS/cm) | 0.20 | 0.20 | 0.30 | 0.30 | 0.05 - 1.5 mS/cm |
| Oil / Grease (ppm) | ND | ND | ND | ND | 10 ppm |
| Fe (ppm) | 3.07 | 7.40 | 9.46 | 1.10 | 0.30 - 1.0 ppm |
| Cr (ppb) | 5.05 | 3.65 | 4.60 | 4.98 | 5.0 ppb |
| Ni (ppb) | 0.09 | 0.03 | 0.07 | 0.01 | 5.0 ppb |
| Pb (ppb) | 0.23 | 0.23 | 0.21 | 0.23 | 5.0 ppb |
| Zn (ppm) | 0.17 | 0.06 | 0.14 | 0.08 | 5.0 - 15.0/5.0 ppm |
| Cd (ppb) | 0.00 | 0.00 | 0.00 | 0.00 | 1.0 ppb |
| Cu (ppm) | 0.03 | 0.00 | 0.02 | 0.00 | 0.5-1.0 ppm |
| Arsenic (ppb) | 1.03 | 0.12 | 0.02 | 0.40 | 5.0 ppb |
| Manganese (ppm) | 0.23 | 0.28 | 0.15 | 0.10 | 0.1- 0.3 ppm |
| Cobalt (ppb) | 0.02 | 0.06 | 0.06 | 0.05 | 3.0 - 5.0 ppb |
| Selenium (ppb) | 0.50 | 0.25 | 0.52 | 0.23 | 0.5 ppb |
| Molybdenum (ppb) | 1.48 | 1.13 | 1.18 | 1.10 | 1.0 - 1.5 ppb |
| Vanadium (ppb) | 3.33 | 3.56 | 2.56 | 2.56 | 5.0 ppb |

This observation indicates that acid tar pit situated at Digboi Refinery has only localised affect on ground water. Ground water around Digboi Refinery did not show high contamination of oil/grease and heavy metals.

Heavy metal contents in soil

Heavy metal content in soil (Table 18) collected from different depth at acid tar pit was within the normal range known for agricultural soils and well below the usual range for FGD sludge, oil ash, Fly ash, bottom ash and coal (Table 19)

Table 19 Heavy metal concentration in soil along with bore wells situated on North, East, South and West side of acid tar pit

| Heavy Metals | Surface | | 50 cm Below Surface | | 100 cm Below Surface | |
|--------------|---------------|------------|---------------------|------------|----------------------|------------|
| | February 2001 | April 2001 | February 2001 | April 2001 | February 2001 | April 2001 |
| Fe (ppm) | 13614.66 | 11045.08 | 14581.00 | 10768.29 | 13571.00 | 12916.76 |
| Cu (ppm) | 59.51 | 38.34 | 77.17 | 29.24 | 72.54 | 55.48 |
| Zn (ppm) | 150.96 | 81.28 | 150.74 | 55.48 | 163.00 | 78.17 |
| Mn (ppm) | 233.79 | 277.63 | 210.36 | 76.90 | 212.96 | 91.76 |
| Ni (ppb) | 2937.00 | 10243.7 | 6137.00 | 3252.07 | 3899.00 | 3412.65 |
| Co (ppb) | 1215.00 | 363.46 | 1923.21 | 90.87 | 1680.00 | 371.85 |
| As (ppb) | 668.00 | 534.11 | 541.00 | 911.07 | 570.00 | 626.55 |
| Pb (ppb) | 1229.00 | 62290.27 | 1566.00 | 47070.69 | 1633.00 | 50792.86 |
| Se (ppb) | 116.77 | 77.07 | 121.21 | 98.48 | 115.00 | 51.38 |
| Cr (ppb) | 98.45 | 5386.11 | 90.94 | 2188.71 | 116.70 | 4626.88 |
| Cd (ppb) | 4.60 | 1352.10 | 8.60 | 420.28 | 5.17 | 387.47 |
| V (ppb) | 5.35 | 1017.90 | 4.81 | 704.70 | 7.24 | 1096.20 |
| Mo (ppb) | 47.00 | 830.57 | 85.56 | 203.68 | 59.71 | 89.68 |



Conclusion

- pH, conductivity and heavy metal concentration in surface and subsurface soils collected adjacent to acid tar pit (near sample bore wells) were well within the known ranges for agricultural / healthy soils.
- pH and conductivity of the water samples of all four bore well situated at acid tar pit were within the permissible limit.
- The heavy metal concentration in ground water at acid tar pit was higher for certain metals like Cr, Pb, Ni and As.
- However, heavy metal concentrations in raw drinking water collected from water supply wells and tanks at Digboi town were within the permissible limits except iron as show in Table 18. There is a seasonal flux in heavy metal concentration in ground water.

- At Digboi petroleum refinery, acid refining of lubricating base oil stock and waxes generate acidic sludge/ tar having different composition and consistency. Disposal of these acidic sludge / tar has been a problem. Since the late 1940's, the acidic sludge / tar that had been generated by Digboi refinery from acid refining of lubricating base oil & wax had been dumped in a location inside the refinery. At that time the environmental issues were not given due consideration nor were there any legislation on it. About 30,000 MT of this solid waste had accumulated at one point of time. The processes available at that time could not be adopted due to peculiar nature of sludge / tar and also due to economic reasons in the past.
- Safe disposal practices shall be adapted for further disposal of the acid tar sludge and long-term storage avoided. Such environmentally defiant and contentious storage practices need to be disposed and biosafe and ecosystem benevolent redemption practices adapted. The pits must bear a cemented/impermeable barrier to prevent the leaching and percolation of the contaminants. However, Digboi Refinery has taken following measures:
 - i) The acid treatment of lubricating base oil has been discontinued since 1982.
 - ii) In the recent past fresh acid sludge / tar generated from acid refining of wax has been disposed off to a private party approved by Pollution Control Board, Assam. Hence, there has been no increase in accumulation of the solid waste.
 - iii) Since June 2001, the acid refining process of wax has been discontinued and replaced by an eco-friendly Wax Hydrofinishing process, thereby, stopping further generation of this solid waste.
 - iv) Digboi refinery is working on reclamation of the Acid Sludge / Tar dumping area and about 40% t 45% of the area has been reclaimed till now. The Acid Sludge / Tar removed from this area is being neutralised, dried and thereafter disposed off either through incineration in the refinery's Captive Incinerator and to a small

extent sold to brick manufacturer for use as fuel in conjunction with coal in brick Kilns.

- Any longstanding and newly generated acid tar sludge must be subjected immediately to bioremediation through available microbial technology using hydrocarbon degrading bacterial consortium. As chemical technology is quite cumbersome and costly, eg. to remove 1 lb of Se 7500 lbs of sludge is generated and shall cost ~ \$4000-8000/-, hence technologically not feasible
- Although, microbial bioremediation technology cures the oil/grease contamination, heavy metals are still caged within the soil matrix and confronts a major threat of re-entrance into the ecosystem if the soil is used for plantation and greening purposes and could still downpour into the water table through seasonal precipitation. Hence, microbial metal immobilisation and bioleaching shall be the next concomitant phase of restoration attempts. Only after this phase the substrate shall be used for plantation and afforestation practices. A technology package could be developed if adequate funding is improvised.
- TERI emphasises on a more permutable approach to evaluate the total spread zone of the polluted water table. TERI proposes a thorough reconnaissance of the upstream and downstream by installation of new monitoring wells and the existing water aquifers/wells under use by the neighbouring community. As the pollution levels are high and could have severe consequences on long term consumption, usage and release onto the ground, the total spread area of the polluted water table shall be mapped and the usage of polluted pockets prevented.
- Adequate and proper measures must be taken to avoid the circulation of polluted ground water in the terrestrial ecosystem.
- Closed loop water refining and recharging approach could be designed and worked out amicably to quench out the contaminants and charge back the mimic-quality water into the table.
- Newer and safer technologies shall be adapted to stop the generation of acid tar sludge.
- Biological and chemical redemption process seems to be a possible and feasible means.

List of abbreviations

| | | |
|------|---|--------------------------------|
| BIS | : | Bureau of Indian Standards |
| WHO | : | World Health Organisation |
| EPA | : | Environment Protection Agency |
| IPC | : | Industrial Pollution Control |
| EQOs | : | Environment Quality Objectives |
| DOE | : | Department of Environment |
| EC | : | European Commission |
| TERI | : | Tata Energy Research Institute |
| TPH | : | Total Petroleum Hydrocarbons |
| BTX | : | Benzene Toluene Xylene |